Thermodynamic Deprotonation of N,N′-Disubstituted Violuric Acid and Thiovioluric Acid in Dioxane-Water Mixtures

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Thermodynamic deprotonation constants (pK_a^T) of diphenyl violuric acid [DPVA], di-*p*-tolyl violuric acid [D-*p*-TVA], di-*m*-tolyl violuric acid [D-*m*-TVA], di-*o*-tolyl violuric acid [D-*o*-TVA], di-*p*-xylyl violuric acid [D-*p*-XVA], di-*m*-xylyl violuric acid [D-*m*-XVA], di-*o*-xylyl violuric acid [D-*o*-XVA], Di-α-napthyl thiovioluric acid [D-α-NTVA] and di-β-napthyl thiovioluric acid [D-β-NTVA] have been determined in different mole fraction of dioxane [0.174-0.350] at 20, 30 and 40 ± 0.10 ºC. The thermodynamic deprotonation constant (pK_a^T) values do not vary linearly with the reciprocal of the dielectric constant of medium, but a plot of pK_a^T *versus* the mole fraction of dioxane is linear at all the given temperatures. The mean ionic radii $r_\pm$ for violurates and thiovioulurate ions, being in the region of 2.15-2.75 Å, slightly increases with dioxane percentages. The values of ΔGº, ΔHº and ΔSº have been evaluated. The effect of temperature, as well as medium effect are briefly discussed.

Key Words: Thermodynamic, N,N′-Disubstituted violuric acid, Thiovioluric acid, Dioxane-water mixtures.

INTRODUCTION

Violuric acid and thiovioluric acid are versatile reagents in the field of analytical chemistry. Analytical applications of this family of compounds have been extensively examined in recent years[1-6]. A knowledge of their deprotonation constants is of intrinsic importance in devising separative and analytical techniques. Moreover, these values are needed for evaluating the complexing ability of these ligands with metal ions. Additionally the thermodynamic parameters so derived greatly help in correlating as well as studying the metal-ligand reactions. With this view, the thermodynamic deprotonation pK_a^T of 1,3-disubstituted violuric acid and thiovioluric acid in different mole fractions of dioxane at 20, 30 and 40 ± 0.01 ºC have been determined and the thermodynamic parameters associated with the deprotonation process are evaluated.

EXPERIMENTAL

Substituted violuric acid and thiovioluric acid were synthesized by the usual procedure reported in the literature[7-8] and recrystallized before use and the purity was checked by elemental analysis, UV and IR spectra. All other chemicals were

of AR or GR-grade. An aqueous solution (10 %) of tetramethylammonium hydroxide (TMAH) titrant was standardized against potassium hydroxide and diluted to 0.1 M, the proportions of dioxane and water being the same as used in preparing the titre solutions. *p*-Dioxane was purified as recommended[9].

The titration procedure for determining the deprotonataion constants was essentially the same as outlined by Albert and Serjeant[10]. Generally, 0.01 M violuric acid and thiovioluric acid were titrated without the addition of inert salt. The measurements of pH were made on an expanded scale pH-meter [ELICO, Model No. pH 821 Hyderabad]. The instrument was standardized against phthalate and borax buffers before and after each titration.

In a thermostated (20, 30 and 40 ± 0.01 ºC) titration vessel, accomodating a glass electrode, a limb of saturated KCl bridge and a microburette of 5.0 mL capacity, 0.5 M of violuric acid and thiovioluric acid in the appropriate dioxane-water compostion was taken and the contents stirred magnetically. The initial volume of the titre solution was 47.5 mL in all cases to allow for the change in the total volume of solution on the addition of titrant[11]. For practical purposes, the error caused by volume correction is almost negligible [less than 0.01 pH unit for the inner five readings of a set of pH titrations] with a maximum error of 0.018 pH unit[12]. About 10 min after the settings, the titration was started by adding 0.5 mL aliquots of 0.1 M TMAH at a time and noting the highest stable pH. The titrations, carried out in duplicate, were reproducible within ± 0.01pH unit.

Calculation

The thermodynamic deprotonation constants pK_a^T values have been determined by the pH titration method using a glass and saturated calomel electrode in cells with a liquid junction potential. The relationship of Van Uitert and Hass[13] was used to determine the H$^+$ concentration from the values read on the pH-meter [B].

$$- \log[H^+] = B + \log U_H^O + \log \gamma_\pm \qquad (1)$$

Values of the correction factor, $\log U_H^O$, were obtained experimentally[14] and those of the mean coefficient [$\gamma_\pm$] were computed by interpolation of the data given by Harned and Owen[15]. Here an assumption has been made that mean activity coefficients are the same on both the molal and molar scales. The deprotonation of violuric acid and thiovioluric acid [HA] in an aqueous medium gives [H$^+$] and violurate or thioviolurate anion [A$^-$] and in such a medium, the equilibrium constant is given by eqn. (2).

$$K_a^T(aq) = \frac{[H^+][A^-]}{[HA]} \cdot \frac{(\gamma_{H^+})(\gamma_{A^-})}{(\gamma_{HA})} \qquad (2)$$

or

$$pK_a^T = -\log[H^+] + \log\frac{[HA]}{[A^-]} + 2\log\left(\frac{1}{\gamma_\pm}\right) \qquad (3)$$

Assuming γ_{HA}, the mean activity coefficient of unionized acid, is unity, the final form of the equation for computing pK_a^T in the dioxane-water mixture is obtained by eqns. 1 and 3.

$$pK_a^T = B + \log U_H^O + \log \frac{[HA]}{[A^-]} + 2\log\left(\frac{1}{\gamma_{\pm}}\right) \tag{4}$$

A correction for hydrolysis of the salt, which may be significant at the end of the titration (*i.e.*, at pH > 10) was applied by substituting $\log \frac{[HA]+[OH^-]}{[A^-]-[OH^-]}$ for $\log \frac{[HA]}{[A^-]}$ in eqns. 3 or 4 hydroxyl ion activity $[OH^-]$ was computed from the relationship[16].

$$[OH^-] = \text{antilog } [B - pK_W]$$

The ionic product of water, pK_W, has been obtained from the data of Agrawal[17] in different dioxane-water mixtures.

The standard change in free energy ΔG^o, enthalpy ΔH^o and entropy ΔS^o associated with the deprotonation equilibrium, *i.e.*

$$HA \rightleftharpoons H^+ + A^-$$
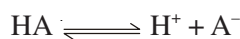
Can be readily evaluated on the basis of eqns. (5)-(7).

$$\Delta G^o = 2.303 \text{ RT } pK_a^T \tag{5}$$

$$\frac{d\log K_a^T}{d(1/T)} = \frac{-\Delta H^o}{4.57} \tag{6}$$

$$\Delta S^o = \frac{\Delta H^o - \Delta G^o}{T} \tag{7}$$

RESULTS AND DISCUSSION

pK_a^T values of violuric acid and thiovioluric acid in different aqueous dioxane media at 20, 30 and 40 ºC are given in Table-1. It is quite evident here that the pK_a^T of these reagents in all media invariably decrease with increasing temperature. The average pK_a^T usually falls within a spread of ± 0.02 but not beyond ± 0.03 in any instance. The empirical data for the mole fraction of dioxane (n_2) and ΔG^o, ΔH^o and ΔS^o values are given in Tables 2 and 3, respectively.

Effect of medium: Acid strength and thus pK_a^T values of acids are influenced by the intrinsic basicity of the solvent. The deprotonation equilibrium for violuric acid and thiovioluric acid is an ionogenic reaction and therefore, the changes in pK_a^T values with dioxane should be accounted for by the electrostatic and specific solvation effects, considering its acid dissociation involving a net increase of ions.

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

TABLE-1
$p\text{K}_a^T$ VALUES OF N-N'-Di SUBSTITUTED VIOLURIC ACID AND
THIOVIOLURIC ACID AT DIFFERENT TEMPERATURES

Acids	Mole fraction of dioxane (n_2)											
	0^a			0.174			0.250			0.350		
	20 ℃	30 ℃	40 ℃	20 ℃	30 ℃	40 ℃	20 ℃	30 ℃	40 ℃	20 ℃	30 ℃	40 ℃
DPVA	4.55	4.40	4.26	5.38	5.25	5.14	5.77	5.65	5.53	6.34	6.20	6.07
D-p-TVA	4.83	4.67	4.52	5.72	5.59	5.48	6.13	5.98	5.87	6.65	6.50	6.38
D-n-TVA	4.46	4.32	4.18	5.29	5.18	5.09	5.64	5.52	5.43	6.13	6.02	5.92
D-o-TVA	4.28	4.14	4.02	4.94	4.85	4.76	5.38	5.27	5.18	5.84	5.72	5.61
D-o-XVA	4.42	4.28	4.13	5.03	4.94	4.85	5.42	5.31	5.22	5.90	5.78	5.68
D-m-XVA	4.76	4.60	4.45	5.62	5.50	5.40	5.98	5.86	5.75	6.53	6.40	6.28
D-p-XVA	4.40	4.27	4.12	5.25	5.15	5.06	5.58	5.47	5.38	6.07	5.96	5.87
D-α-NTVA	4.92	4.83	4.73	5.81	5.70	5.59	6.25	6.10	5.99	6.76	6.61	6.49
D-β-NTVA	4.78	4.69	4.61	5.63	5.53	5.42	5.98	5.89	5.80	6.55	6.44	6.35

0^a: Extrapolated values at 0 % dioxane.

A decrease in the dielectric constant of the reaction medium enhances the electrostatic forces between the oppositely charged ions and thus facilitates the formation of molecular species[18] which should increase the $p\text{K}_a^T$ (Table-1). This prediction has been simply confirmed for other reagents on the basis of previous studies[19-21].

Gurney[22] and others[23] has proposed that the free energy of deprotonation of acids in solutions at its infinite dilution might be expressed as the sum of an electrostatic term [el.] sensitive to the environment and a nonelectrostatic term [nonel.] insensitive to the environment and independent of temperature.

$$\Delta G^o_{diss.} = \Delta G^o_{el.} + \Delta G^o_{nonel.} \tag{8}$$

If the electrostatic part is expressed by Born's formula[24], eqn. (8) takes the from

$$\Delta G^o_{el.} = \frac{Ne^2}{2D}\left[\frac{1}{r_+} + \frac{1}{r_-}\right]$$

where r_+ and r_- denote the radii of the solvated ions and D is the dielectric constant of the medium[25,26]. Hence,

$$\Delta G^o_{diss.} = \Delta G^o_{nonel.} + \frac{Ne^2}{2D}\left[\frac{1}{r_+} + \frac{1}{r_-}\right]$$

Further, as $\Delta G^o_{diss.} = 2.303\ RT\ p\text{K}_a^T$.

The equation simplifies as

$$p\text{K}_a^T = \frac{\Delta G^o_{nonel.}}{2.303\ RT} + \frac{Ne^2}{4.606\ RTD}\left[\frac{1}{r_+} + \frac{1}{r_-}\right] \tag{9}$$

Conventionally, $p\text{K}_a^T$ is plotted against 1/D assuming $\Delta G^o_{nonel.}$ to be independent of solvent when values of substituted violuric acid and thiovioluric acid are plotted against 1/D. It is observed that the plots have a distinct curvature. It seems evident that non-electrostatic factors exert a considerable influence on the deprotonation of violuric acid and thiovioluric acid.

TABLE-2
EMPIRICAL CORRELATION OF pK_a^T WITH MOLE FRACTION OF DIOXANE (n_2)

Acid	Temp. (ºC)	$pK_a^T = mn_2 + C$			Graphically	
		Least squares method			m	C
		m	C	r		
DPVA	20	5.60	4.59	1.00	5.58	4.56
	30	5.58	4.48	1.00	5.56	4.45
	40	5.57	4.35	1.00	5.57	4.34
D-*p*-TVA	20	5.08	4.81	1.00	5.07	4.80
	30	5.06	4.73	1.00	5.05	4.72
	40	5.07	4.60	0.99	5.05	4.61
D-*n*-TVA	20	4.57	4.48	1.00	4.56	4.46
	30	4.55	4.35	0.99	4.54	4.38
	40	4.58	4.30	1.00	4.55	4.29
D-*o*-TVA	20	4.55	4.29	1.00	4.53	4.28
	30	4.54	4.17	0.99	4.52	4.18
	40	4.53	4.10	1.00	4.51	4.09
D-*o*-XVA	20	5.30	4.45	1.00	5.27	4.44
	30	5.28	4.30	0.99	5.25	4.32
	40	5.27	4.20	0.99	5.26	4.22
D-*m*-XVA	20	5.50	4.75	1.00	5.48	4.74
	30	5.49	4.68	1.00	5.48	4.65
	40	5.48	4.55	1.00	5.47	4.54
D-*p*-XVA	20	4.74	4.42	1.00	4.72	4.40
	30	4.70	4.31	1.00	4.71	4.30
	40	4.72	4.19	0.99	4.70	4.20
D-α-NTVA	20	5.61	4.95	0.99	5.59	4.96
	30	5.59	4.88	1.00	5.56	4.88
	40	5.58	4.78	1.00	5.55	4.79
D-β-NTVA	20	5.59	4.61	0.99	5.56	4.63
	30	5.59	4.55	1.00	5.56	4.56
	40	5.57	4.46	1.00	5.53	4.47

TABLE-3
$\Delta G°$, $\Delta H°$ AND $\Delta S°$ VALUES FOR N,N'-DISUBSTITUTED VIOLURIC
ACID AND THIOVIOLURIC ACID AT 30 ºC

Acids	Mole fraction of dioxane (n_2)											
	0[a]			0.174			0.250			0.350		
	$\Delta H°$	$\Delta G°$	$-\Delta S°$	$\Delta H°$	$\Delta G°$	$-\Delta S°$	$\Delta H°$	$\Delta G°$	$-\Delta S°$	$\Delta H°$	$\Delta G°$	$-\Delta S°$
DPVA	4.38	6.14	5.80	4.75	7.25	8.25	4.77	7.80	10.00	5.11	8.56	11.38
D-*p*-TVA	5.02	6.52	4.95	5.39	7.72	7.68	5.40	8.26	9.43	5.74	8.98	10.69
D-*n*-TVA	4.02	6.02	6.66	4.38	7.15	9.14	4.41	7.62	10.59	4.70	8.31	11.91
D-*o*-TVA	3.38	5.77	7.88	3.68	6.70	9.96	3.70	7.28	11.81	3.97	7.90	12.97
D-*o*-XVA	3.72	5.96	7.39	4.03	6.82	9.20	4.05	7.33	10.82	4.35	7.98	11.98
D-*m*-XVA	4.54	6.42	6.20	4.87	7.59	8.97	4.88	8.09	10.59	5.18	8.84	12.08
D-*p*-XVA	3.99	5.94	6.43	4.30	7.11	9.27	4.32	7.55	10.66	4.60	8.23	11.98
D-α-NTVA	5.20	6.66	4.83	5.57	7.87	7.50	5.59	8.42	9.35	5.93	9.12	10.53
D-β-NTVA	7.03	6.47	7.03	4.98	7.63	8.75	5.02	8.14	10.27	5.32	8.89	11.75

$\Delta H°$ and $\Delta G°$ in Kcal mol^{-1}; $\Delta S°$ in cal mol^{-1} K^{-1}; 0[a] Extrapolated values at 0 % dioxane.

Mole fraction of dioxane: According to Glover[27] a consideration of the direct participation of the solvent in the acid deprotonation should lead to a better understanding of the compositions of solvent as well as of ion solvates. For instance, such a participation is quite evident from essentially straight line plots of pK_a^T *vs.* n_2 in several examples[28].

For violuric acid and thiovioluric acid, the change in pK_a^T with mole fraction of dioxane (n_2) is of considerable magnitude. Generally, the difference in pK_a^T in aqueous medium ($n_2 = 0$) and aqueous dioxane medium [$n_2 = 0.350$] is of the order of 1.8-2.50 pK_a^T units. When pK_a^T values of these violuric acid and thiovioluric acid are plotted against n_2, straight line relationship are encountered (Fig. 1). The experimental values of pK_a^T indicate a maximum deviation from linearity of the order of 0.05 or about 0.5 % in pK_a^T.

The goodness of fit in these instances was judged by calculating the correlation coefficient (m) defined by

$$m = \frac{\Sigma(x - \bar{x})(y - \bar{y})}{[\Sigma(x - \bar{x})^2 \Sigma(y - \bar{y})^2]^{1/2}}$$

where $\bar{x}$ and $\bar{y}$ are the mean values of $x(pK_a^T)$ and $y(n_2)$, respectively. The summations are extended to all pairs (x, y) available. Linear proportionality is readily indicated between the two variables[29] when the values of m is + 1.0.

Since the value of m is nearly +1.0 at 20, 30 and 40 ºC for all the substituted violuric acid and thiovioluric acid (Table-2). It implies that there is quite a high probability of a linear relationship between pK_a^T and n_2. A similar behaviour is found for several other acids[28] in aqueous dioxane. Likewise linear proportionality is also obtained for some other mixed water solvents *e.g.*, acetic acid, propionic acid, butyric acid and benzoic acid in methanol-water mixture[30].

Mean ionic radii ($r_\pm$): To provide an electrostatic interpretation of the medium effect concerning an deprotonation process, Born's solvation energy eqn. 9 has been simplified by King[31] as

$$\Delta pK_a^T = pK_{a(s)}^T - pK_{a(w)}^T = \frac{Ne^2}{2.303\,RTr_\pm}\left[\frac{1}{D_S} - \frac{1}{D_W}\right] \tag{10}$$

where $r_\pm$, mean ionic radii, is equal to

$$\frac{2}{r_\pm} = \frac{1}{r_\pm} + \frac{1}{r_-}$$

Values of $r_\pm$ have been computed *via* eqn. 10 at different dioxane percentage and are in the range 2.15-2.75 Å. It is obvious from this computation process that the values of $r_\pm$ increase slightly with aqueous dioxane concentrations. It is difficult to explain this variation with change in solvent composition. Similar increase in $r_\pm$ values has been encountered while studying the acids dissociation of other acids[32,33].

Values of $r_\pm$ have also been evaluated graphically from equation[9]. The slope of the plot pK_a^T *vs.* $1/D$ is equal to $\dfrac{Ne^2}{2.303\,RTr_\pm}$, where all the terms except $r_\pm$ are known. The values thus calculated are in the range 2.10-2.18Å which seems to be reasonable if the effective size of the substituted violurate and thioviolurate ions is regarded as being largely determined by the charged O^- group. Following a similar study, the radius of the propionate ion has been estimated[34] to be around 2.3 Å. Ohtaki[35] has, however, pointed out the limitations of the Born equation for the accurate estimation of the ionic radii. Graphical determination of $r_\pm$ may therefore be in some error compared with the previous method, but the values are still within the range.

Thermodynamic functions for ionic equilibria: The pK_a^T values have been determined with a precision of ± 0.02 to ± 0.03 and hence the error in ΔG^o is believed to be close to ± 0.03 and ± 0.04 Kcal mol^{-1}. The values of ΔS^o given in Table-3 are accurate to ± 0.20 cal mol^{-1} k^{-1}.

The positive value of ΔH^o found in aqueous as well as aqueous-dioxane mixtures for all substituted violuric acid and thiovioluric acid proves that their acid dissociation at temperatures upto 40 °C is endothermic. The positive value of ΔH^o encountered here may be ascribed to the breaking of the covalent bond between hydrogen and oxygen atoms of -OH group of violuric acid and thiovioluric acid. Further it is evident that the magnitude of change in ΔH^o with solvent composition is relatively small and falls within the range of experimental error. It is because of this that slopes of straight lines in the plots of pK_a^T against n_2 (Fig. 1) do not differ markedly and are nearly the same and parallel at these temperatures for all the violuric acid and thiovioluric acid.
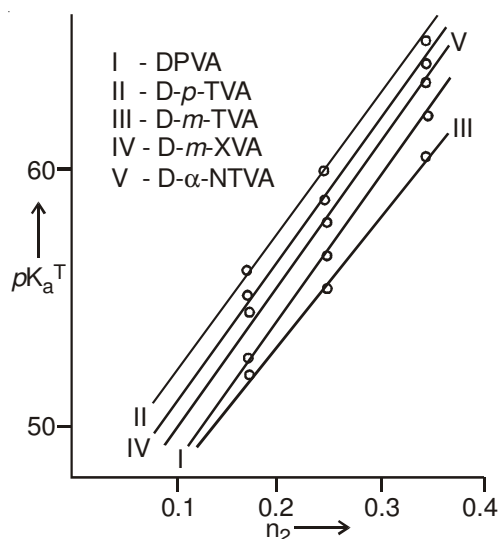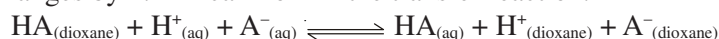

Fig. 1. Plots between mole fraction of dioxane (n_2) and pK_a^T values at 30 °C

The values of ΔS^o are found to decrease with increase in dioxane content of the solvent medium for all the violuric acid and thiovioluric acid, thereby proving that it is dependent of solvent composition. The negative value of entropy has been explained as arising due to deprotonation of the ligand since the sum of the total of the number of water molecules 'bound' is more than the water molecules originally accompanying the undissociated violuric acid and thiovioluric acid.

When the acid dissociates in two media, the free energy change for the transfer reaction from one medium to the other is given by 2.303 RT ΔpK_a^T. For instance with DPVA, $\Delta G^o_{(aq)}$ and $\Delta G^o_{(n_2 = 0.174)}$ are 6.14 and 7.25 Kcal mol^{-1}, respectively at 30 ºC and ΔG^o changes by 1.11 Kcal mol^{-1} in the transfer reaction.

$$HA_{(dioxane)} + H^+_{(aq)} + A^-_{(aq)} \rightleftharpoons HA_{(aq)} + H^+_{(dioxane)} + A^-_{(dioxane)}$$

and this results in a change of 2.45 cal mol^{-1} in entropy.

ΔpK_a^T (S-W) values $i.e.$, pK_a^T (S) – pK_a^T (W), [where S and W refer to mixed solvents and water, respectively] of violuric acid and thiovioluric acid at 30 ºC are given in Table-4. The change in pK_a^T (S-W) which is found to be different for the different acids for the same percentage of dioxane is probably due to the presence of different substituents which cause a great change in the distribution of electron density in the ring and hence the electron density at any particular point is also affected.

TABLE-4
DpK_a^T (S – W) = DpK_a^T (S) – DpK_a^T (W)

Acid	Mole fraction of dioxane (n_2)								
	0.174			0.250			0.350		
	20 ºC	30 ºC	40 ºC	20 ºC	30 ºC	40 ºC	20 ºC	30 ºC	40 ºC
DPVA	0.83	0.85	0.88	1.22	1.25	1.27	1.79	1.80	1.81
D-p-TVA	0.89	0.92	0.96	1.30	1.31	1.35	1.82	1.83	1.86
D-n-TVA	0.83	0.86	0.91	1.18	1.20	1.25	1.67	1.70	1.74
D-o-TVA	0.66	0.71	0.76	1.10	1.13	1.18	1.56	1.58	1.61
D-o-XVA	0.61	0.64	0.72	1.00	1.03	1.09	1.48	1.50	1.55
D-m-XVA	0.86	0.90	0.95	1.22	1.26	1.30	1.77	1.80	1.83
D-p-XVA	0.85	0.88	0.94	1.18	1.20	1.26	1.67	1.69	1.75
D-α-NTVA	0.93	0.88	0.87	1.35	1.28	1.27	1.86	1.79	1.78
D-β-NTVA	0.86	0.85	0.82	1.21	1.21	1.78	1.78	1.76	1.75

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